THE ELECTROCHEMICAL PROPERTIES OF SILVER NANOPARTICLES AT THE GRAPHITE ELECTRODE

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ЭЛЕКТРОХИМИЧЕСКИЕ СВОЙСТВА НАНОЧАСТИЦ СЕРЕБРА НА ГРАФИТОВОМ ЭЛЕКТРОДЕ

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Аннотация. *В настоящей работе было показано, что наночастицы серебра, полученные при молярном соотношении реагентов [$AgNO_3$]: [$Na_3C_6H_5O_7$] = 1:1 в условии отсутствии стабилизатора с высоким молекулярным весом, обладают максимальной электрохимической активностью, что связано с неполным восстановлением ионов серебра. Этот факт соотносится с данными УФ-спектроскопии. Наночастицы серебра, полученные в избытке восстановителя при молярном соотношении реагентов [$AgNO_3$]: [$Na_3C_6H_5O_7$] = 1:5 электрохимически неактивны, что также соответствует данным УФ-спектроскопии. Увеличение активности наночастиц серебра происходит в условии увеличения диапазона изменения потенциала, что может быть вызвано образованием перекиси водорода, обладающей активационной способностью. В данной работе установлены оптимальные условия, в которых наночастицы серебра являются наиболее электрохимически активны.*

The interest of the researchers to the nanoparticles of colloidal silver (NP Ag) has recently increased due to their catalytic activity, antibacterial properties, and the possibility to use in electrochemical sensors and biosensors. Besides, the particles under discussion display high sensitivity, selectivity and low cost. However, the study on the electrochemical behavior of the system on Ag indicator electrodes, as well as their status in the solution still remains a blank research area. The mechanism of their formation is not completely understood, therefore, the aim of this work is to study both characteristics of the electrochemical oxidation and reduction of the NP Ag on the surface of a graphite electrode (GE).

The silver sols were prepared with chemical reduction of $AgNO_3$ with sodium citrate, being at the same time a reducing agent and a stabilizer at a different molar reactant ratio $AgNO_3$: $Na_3C_6H_5O_7$ = 1: 1, 1: 3, 1: 5. The obtained mixtures were heated and boiled until the characteristic color appeared. (Table 1).

Scanning electron microscopy (JSM-5500), spectrophotometry (2800 UV / VIS Spectrophotometer), cyclic voltammetry (TA-2, Tomsk) with a three-electrode cell were used to determine the characteristic of NP Ag. GE was used as an working electrode, silver chloride electrodes were used as auxiliary reference electrodes.

The surface purification of the GE was accomplished 1) mechanically and 2) electrochemically. The GE surface was modified by NP Ag under the following conditions: E = -0,8 V, t = 300 s. The voltammetric measurements were made under the following sweep ranges: E = -1,0 - +0,5 V; -1,0 – 1,0 V; -1,0 – 1,5 V. Supporting electrolytes were 0,1 M NaOH, 0,1 M phosphate buffer (pH 6,86), 0,1 M $NaNO_3$. The listed solutions were prepared with bidistilled water.

Table 1

Conditions for obtaining silver sols

№	Molar ratio $AgNO_3$:$Na_3C_6H_5O_7$	Boiling time, min	Colouring
1	1:1	20	yellow
2	1:3	20	Light Yellow
3	1:5	40	yellow
4	1:1	40	brown
5	1:3	40	brown

It is known that the physical and chemical properties are determined by the size and shape of silver particles, therefore, their shape depends on the molar ratio of the reactants [Ag] and [$Na_3C_6H_5O_6$] .

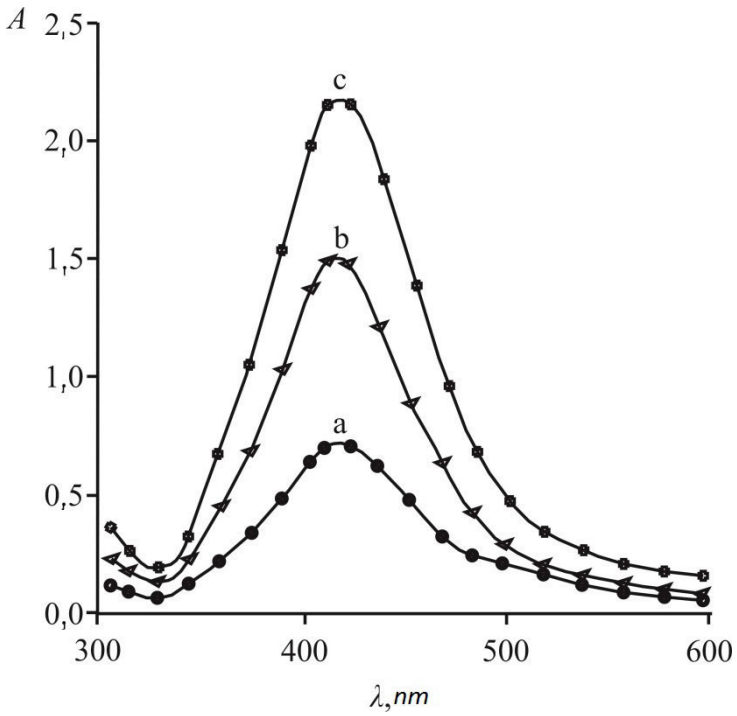

Fig.1 Optical spectra of nanoparticles of Ag, obtained with a molar ratio $AgNO_3$: $Na_3C_6H_5O_7$ = 1: 1 (a) 1: 3 (b), 1: 5 (c)

The optical spectra of silver sols (graphs a, b, c, Fig. 1) obtained in different conditions are typical absorption bands of NP Ag with λ = 416 nm – corresponding to the plasmon absorption band of NP Ag. The

intensity of the absorption spectrum in the silver sol decreases in the series: [Ag]: [$Na_3C_6H_5O_7$] = 1: 5> 1: 3> 1: 1. The intensity of the spectrum decreases because concentration of sodium citrate decreases, therefore, the reduction process efficiency and amount of reduced ions decrease too.

It was shown that NP Ag, obtained with a molar ratio of the reactants [$AgNO_3$]: [$Na_3C_6H_5O_7$] = 1: 5, shows almost no electrochemical activity in 0,1M NaOH (Fig. 2, graphs c), and the activity decreases in the NP Ag number of the molar ratio [Ag]: [$Na_3C_6H_5O_7$]: 1: 1> 1: 3> 1: 5. This is due to the fact that an excess of sodium citrate leads to complete recovery of silver ions from the sol (1: 5). It was shown that NP Ag obtained with a molar ratio [$AgNO_3$]: [$Na_3C_6H_5O_7$] = 1: 1, is electrochemically active during all the test. NP Ag is the most electrochemically active in 0,1M NaOH.

If the potential sweep range increases, the electromechanical activity of all studied samples increases too, which is probably due to formation of H_2O_2, having activating ability.

Thus, the physicochemical properties of NP Ag were investigated. In excess of sodium citrate ([$AgNO_3$]: [$Na_3C_6H_5O_7$] = 1: 5), the intensity of the absorption spectrum increases while the electrochemical activity of these particles decreases. With an equal molar ratio of reactants([Ag]: [$Na_3C_6H_5O_7$] = 1: 1), the values of the absorption spectrum intensity tend to be low. In the last case, the maximum of electrochemical activity is observed. It is associated with incomplete recovery of the silver ions. The optimal conditions when the NP Ag displays the highest electrochemical activity are the following: molar ratio [$AgNO_3$]: [$Na_3C_6H_5O7$] = 1: 1, 0,1 M NaOH, t = 300 s, the range of potential variation of -1,0 to + 1,5 V.

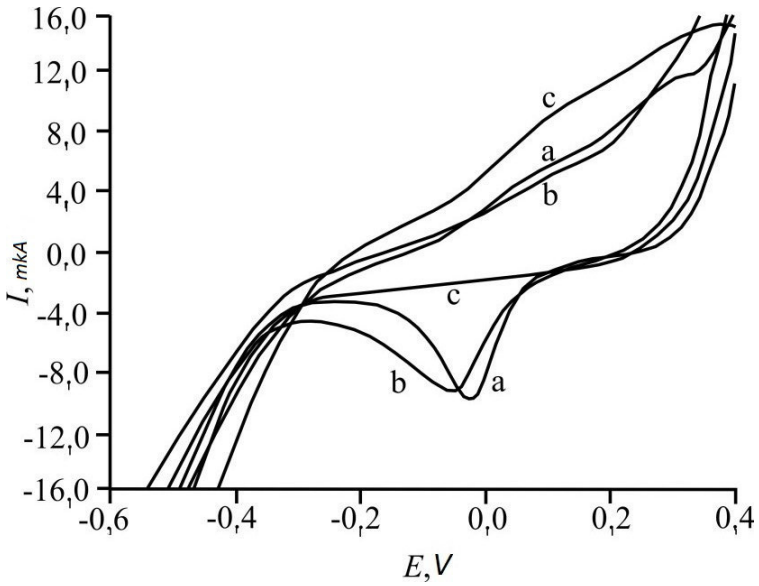

Fig. 2. Cyclic voltammograms of NP Ag, obtained at [AgNO3]: [Na3C6H5O7] = 1: 1 (a), 1: 3 (b), 1: 5 (c). Conditions

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